

AMENDMENTS TO THE CLAIMS

1. (Currently amended) A ~~time-temperature~~time-temperature indicator for indicating a temperature change over time, comprising:

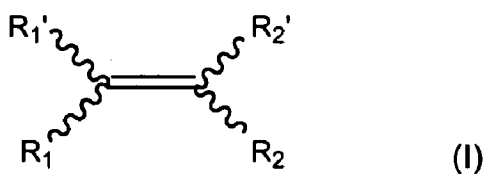
(a) at least one indicator compound in a first isomeric form, which is converted into a second isomeric form of said indicator compound in a valence isomerization reaction without migration of an atom or chemical group attached to said indicator compound in a time and temperature dependent manner, wherein the formation of the second isomeric form is detectable by monitoring a physical characteristic of the first isomeric form or the second isomeric form of the indicator,

(b) a reference scale for evaluating the degree of decoloration or coloration, and

(c) a protector that prevents renewed photo-induced coloration of the indicator or a cover support designed to avoid photo recharging or photo bleaching.

2. (Original) The time-temperature indicator of claim 1, wherein the at least one indicator compound is a diarylethene or a spiroaromatic compound.

3. (Currently amended) The time-temperature indicator of claim 2, wherein the diarylethene is a compound of Formula (I)



wherein:

~~R1 and R2~~ R₁ and R₂ each independently represent C6-C14 aryl, C4-C12 heteroaryl, conjugated heterocyclic; wherein said heteroaryl and conjugated heterocyclic may contain one to three heteroatoms selected from the group consisting of N, O, and S; and wherein said aryl, heteroaryl, or conjugated heterocyclic may be substituted by one or more halogen, hydroxyl, thiol, amino, C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, cyano, nitro, sulfo, -CH=CH-CN, azido, or amido;

~~R1' and R2'~~ R₁' and R₂' each independently represent H, cyano, nitro, sulfo, hydroxyl, thiol, -CH=CH-CN, or amido; or substituted or unsubstituted C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic; or ~~R1' and R2'~~ R₁' and R₂' together with the carbon atoms to which they are attached form a C5-C8 carbocyclic ring or a C4-C7 heterocyclic ring containing one to three endocyclic or exocyclic heteroatoms selected from the group consisting of N, O, and S; said N heteroatom may be further substituted by H, or by one or two substituted or unsubstituted groups selected from the group consisting of C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, hydroxyl, and -CH=CH-CN; when said N heteroatom is tetrasubstituted it is positively charged and is associated with an anion selected from the group consisting of organic and inorganic anions, and optionally wherein said C5-C8 carbocycle is substituted by one or more halogen, ~~preferably by one or more fluoro atoms~~; and optionally

~~R1, R1', R2 and R2'~~ R₁, R₁', R₂ and R₂' each independently represent a charged group or a group substituted by another group having a charge; said charge may be localized or delocalized and may be positive or negative;

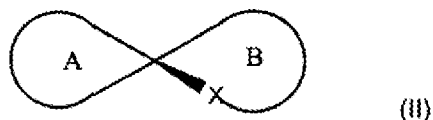
and wherein said ~~R1 and R2~~ R₁ and R₂ are in a cis or trans conformation.

4. (Previously presented) The time-temperature indicator of claim 3, wherein the diarylethene is

- (a) a symmetric diarylethene selected from the group consisting of 1,2-dicyano-1,2-bis(2,4,5-trimethylthiophene-3-yl)ethane (1); 2,3-bis(2,4,5-trimethylthiophene-3-yl) maleic anhydride (2); 1,2-bis(2-cyano-1,5-dimethyl-4-pyrrolyl)perfluorocyclopentene (3); and 1,2-bis(2,4-dimethyl-5-phenylthiophene-3-yl)perfluorocyclopentene (4); or
- (b) an asymmetric diarylethene selected from the group consisting of 2-(1,2-dimethyl-

3-indolyl)-3-(2,4,5-trimethyl-3-thienyl) maleic anhydride (5); and 2-(methoxybenzo[b]thiophene-3-yl)-3-(1,2-dimethyl-3-indolyl) maleic anhydride (6).

5. (Currently amended) The time-temperature indicator of claim 2, wherein the spiroaromatic compound is a compound of Formula (II):



wherein:

ring A represents a C5-C8 carbocycle, C4-C7 heterocycle containing at least one heteroatom selected from the group consisting of N, O, and S; said N heteroatom may be further substituted by one or two groups selected from the group consisting of C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, hydroxyl, and -CH=CH-CN; when said N heteroatom is tetrasubstituted it is positively charged and is associated with an anion selected from the group consisting of organic ~~or~~ and inorganic anions; said C5-C8 carbocycle or C4-C7 heterocycle may be substituted by one or more of the groups selected from the group consisting of halogen, C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, cyano, nitro, sulfo, hydroxyl, thiol, -CH=CH-CN, azido, amido and amino;

ring B represents a substituted or unsubstituted heterocycle containing at least one heteroatom X, said X being selected from the group consisting of N, O, and S; wherein said N atom may be further substituted by one or two groups selected from the group consisting of C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, hydroxyl, ~~or~~ and CH=CH-CN; when said N heteroatom is tetrasubstituted it is positively charged and is associated with an anion selected from the group consisting of organic ~~or~~ and inorganic anions;

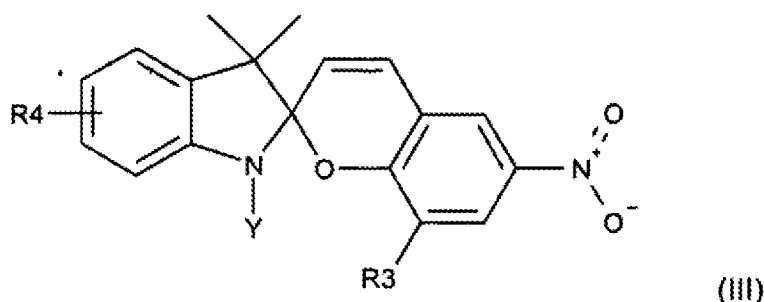
and wherein said ring B may contain one or more endocyclic double bonds and is optionally substituted by one or more halogen;

said rings A and B may be fused to one or more substituted or unsubstituted carbocycle, C4-C14 heterocycle, C6-C14 aryl or C4-C14 heteroaryl ring system;

and wherein the compounds of Formula H-(II) may be neutral, charged, multiply charged, positively charged having an external anion, negatively charged having an external cation or zwitterionic.

6. (Previously presented) The time-temperature indicator of claim 5, wherein the spiroaromatic compound is a spiropyran derivative.

7. (Currently amended) The time-temperature indicator of claim 5, wherein the spiropyran derivative is a derivative of 1',3',3'-trimethyl-6-nitro-spiro(2H-1-benzopyran-2,2'-2H-indole) of Formula (III):



wherein:

R3 is selected from the group consisting of H, halogen, C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, and azido; wherein said alkyl, alkenyl, alkynyl, aryl, heteroaryl, and non-aromatic carbocycle may be substituted by one or more group selected from the group consisting of halogen, hydroxyl, thiol, amino, alkoxy, nitro, azido, and sulfo;

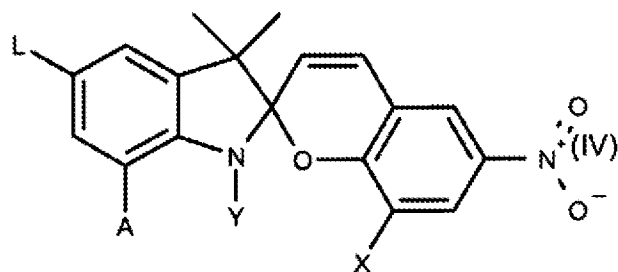
R4 is selected from the group consisting of C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl,

C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, hydroxyl and -CH=CH-CN; and

Y is selected from the group consisting of C1-C25 alkyl and C7-C15 aralkyl, wherein said alkyl and aralkyl is optionally substituted by one or more halogen.

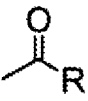
8. (Previously presented) The time-temperature indicator of claim 5, wherein the spiroaromatic compounds include at least one of the following: spirooxazine or its derivatives, spironaphthoxazine or its derivatives, and spiroindolinopyridobenzoxazine or its derivatives.

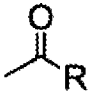
9. (Withdrawn) A spiroaromatic compound of general Formula (IV):



wherein

A and L are independently of each other selected from the group consisting of H, halogen, C2-

C12 alkenyl, C2-C12 alkynyl and , wherein R is C1-C6 alkyl, C1-C6 alkoxy, C6-C14 aryl

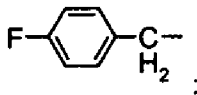
and C7-C15 aralkyl; wherein said alkenyl, alkynyl and , may be substituted by one or more group selected from halogen, hydroxyl, thiol, amino, alkoxy, nitro, azido, sulfo, aryl and heteroaryl;

Y is selected from the group consisting of C1-C25 alkyl and C7-C15 aralkyl, wherein said alkyl and aralkyl is optionally substituted by one or more halogen; and

X is C1-C6 alkoxy or L;

with the proviso that Y is not n-propyl when L, A and X are hydrogen.

10. (Withdrawn) The spiroaromatic compound of claim 9, wherein L is hydrogen, Cl, Br or I;



Y is methyl, n-propyl, n-octadecyl or

X is hydrogen or methoxy; and

A is hydrogen;

with the proviso that Y is not n-propyl when L and X are hydrogen.

11. (Withdrawn) A printing ink or printing ink concentrate, comprising the spiroaromatic compound of claim 9.

12. (Withdrawn) A high molecular weight material, comprising the spiroaromatic compound of claim 9.

13. (Currently amended) A method of manufacturing ~~a~~ the time-temperature indicator of claim 1, comprising the steps of

- (a) embedding in or atop a matrix ~~said~~ at least one indicator compound; ~~and~~
- (b) inducing the formation of a metastable state of said embedded ~~at least one~~ indicator compound; and
- (c) covering the time-temperature indicator with a cover support designed to avoid photo recharging and/or photo bleaching.

14. (Cancelled)

15. (Previously presented) The time-temperature indicator of claim 6, wherein the spiropyran derivative is selected from the group consisting of 1',3',3',8-tetramethyl-5-hydroxymethyl-spiro(2H-pyrano[2,3-c]pyridine-2,2'-2H-indole) and 1',3',3',8-tetramethyl-spiro(2H-pyrano[2,3-c]pyridine-2,2'-2H-indole).

16. (Previously presented) The time-temperature indicator of claim 7, wherein in Formula (III) Y is selected from the group consisting of C1-C25 alkyl and C7-C15 aralkyl, wherein said alkyl and aralkyl are substituted by one or more fluorine.

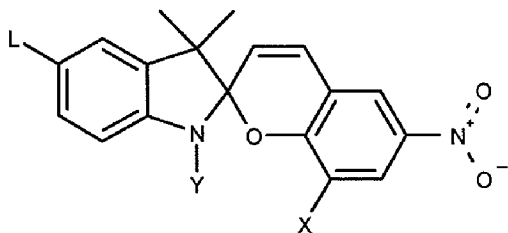
17. (Withdrawn) A spiroaromatic compound of claim 9, wherein in Formula (IV) Y is selected from the group consisting of C1-C25 alkyl and C7-C15 aralkyl, wherein said alkyl and aralkyl are substituted by one or more fluorine.

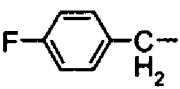
18. (Withdrawn) A printing ink or printing ink concentrate, comprising the spiroaromatic compound of claim 10.

19. (Withdrawn) A high molecular weight material, comprising the spiroaromatic compound of claim 10.

20. (Cancelled)

21. (Previously presented) The time-temperature indicator of claim 2, wherein the spiroaromatic compound has the formula



wherein L is hydrogen, Y is  and X is methoxy.

22. (New) A packaging material or a label that comprises a time-temperature indicator for indicating a temperature change over time, said time temperature indicator comprising at least one indicator compound in a first isomeric form, which is converted into a second isomeric form of said indicator compound in a valence isomerization reaction without migration of an atom or chemical group attached to said indicator compound in a time and temperature dependent manner, wherein the formation of the second isomeric form is detectable by monitoring a physical characteristic of the first isomeric or the second isomeric form of the indicator, and a protector that prevents renewed photo-induced coloration of the indicator or a cover support designed to avoid photo recharging or photo bleaching.

23. (New) The time-temperature indicator of claim 3, wherein R_1' and R_2' together with the carbon atoms to which they are attached form a C5-C8 carbocyclic ring, wherein the C5-C8 carbocyclic ring is substituted by one or more fluorine atoms.